Simple quantitative estimate of the derivative discontinuity of the exchange-correlation functional in atoms and polymers

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Abstract

The derivative discontinuity of the exchange-correlation functional of density-functional theory is cast as the difference of two types of electron affinities. We approximately evaluate this difference via ordinary Kohn-Sham calculations, obtaining estimates of the discontinuity for light atoms and for polyacetylene oligomers. The discontinuity is found to be quite large (typically several eV), and significantly and consistently improves the agreement of the calculated fundamental energy gap with the experimental gaps. For atoms, the error of the HOMO-LUMO gap is reduced in this way by more than one order of magnitude.

Key words: density-functional theory, energy gap, derivative discontinuity, polymers

From spectroscopy to transport, there is hardly any property of a quantum many-particle system that does not in some way depend on whether there is a gap in the energy spectrum, and what the size of this gap is. The fundamental gap is a ground-state property of a many-body system, defined as $E_g = [E(N-1) - E(N)] - [E(N) - E(N+1)]$, where $E(N-1) - E(N)$ is the energy change upon removing the N'th particle from the N particle system, $E(N) - E(N+1)$ that upon removing the $N+1$st particle from the $N+1$ particle system, and the $E(N)$ are total ground-state energies. In a noninteracting system this definition reduces to the HOMO-LUMO gap between single-particle levels. In solids, the particle-removal energies are related to the chemical potential, and

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for finite systems they are given by the ionization energy and electron affinity, respectively.

Density-functional theory (DFT) [1,2] provides, in addition to the ground-state density and related quantities, also a set of single-particle eigenvalues, the so-called Kohn-Sham (KS) spectrum. The difference between the energy of the highest occupied and lowest unoccupied of these single-particle levels is the KS HOMO-LUMO gap in finite systems, or the KS bandstructure gap in extended solids. It is well known that neither the KS nor the Hartree-Fock HOMO-LUMO gap correspond to the experimental gap, the former typically being too small and the latter too large.

Generally, one can write $E_g = E_g^{KS} + \Delta_{xc}$, which defines Δ_{xc} as the difference between the exact fundamental gap and the exact KS HOMO-LUMO gap. In open systems, all three quantities in this definition are related to derivative discontinuities of universal density functionals [3,4,5]. The fundamental gap is the derivative discontinuity of the total energy

$$E_g = \left.\frac{\delta E[n]}{\delta n(\mathbf{r})}\right|_{N+\eta} - \left.\frac{\delta E[n]}{\delta n(\mathbf{r})}\right|_{N-\eta}, \tag{1}$$

the KS HOMO-LUMO gap that of the noninteracting kinetic energy

$$E_g^{KS} = \left.\frac{\delta T_s[n]}{\delta n(\mathbf{r})}\right|_{N+\eta} - \left.\frac{\delta T_s[n]}{\delta n(\mathbf{r})}\right|_{N-\eta}, \tag{2}$$

and the remaining piece, Δ_{xc}, that of the xc energy

$$\Delta_{xc} = \left.\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right|_{N+\eta} - \left.\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right|_{N-\eta} = v_{xc}^{+}(\mathbf{r}) - v_{xc}^{-}(\mathbf{r}). \tag{3}$$

In these equations η stands for an infinitesimal variation of the system's particle number. Equation (3) shows that Δ_{xc} is a system-dependent shift of the xc potential $v_{xc}(\mathbf{r})$ as it passes from the electron-poor to the electron-rich side of integer N.

Theses three relations are useless to calculate gaps from most currently available approximate density functionals, which typically have no discontinuities. For two of the three quantities above, alternative ways of calculation, more useful in practice, are widely known. Total energies are calculated easily from DFT, so that one can employ the definition of ionization energy $I = E(N-1) - E(N)$ and electron affinity $A = E(N) - E(N+1)$ to calculate

the fundamental gap from

$$E_g = E(N+1) + E(N-1) - 2E(N) = I - A. \tag{4}$$

Single-particle energies are obtained from the KS equation, as a byproduct of calculating the total energies, and yield the KS HOMO-LUMO gap

$$E_g^{KS} = \epsilon_{N+1}(N) - \epsilon_N(N), \tag{5}$$

where $\epsilon_M(N)$ denotes the M'th eigenvalue of the N-electron system. The third term, the xc discontinuity Δ_{xc}, has resisted all attempts of describing it directly by common density functionals, such as LDA and GGA, which are continuous as a function of N and thus have no xc discontinuity. Indirect calculation of Δ_{xc} by subtracting (5) from (4) requires separate self-consistent calculations for the N, $N-1$ and $N+1$-particle systems, and involves numerical differences of numbers that individually are much larger than Δ_{xc}. For both of these reasons this becomes impractical for larger systems. In practice, the contribution of Δ_{xc} to the gap is hard to estimate.

In atomic physics and quantum chemistry, the importance of a nonzero derivative discontinuity Δ_{xc} for chemical hardness is well known [2,6]. Neglect of Δ_{xc} has also been shown to lead to large errors in the calculation of Rydberg excitations [7,8], charge-transfer processes and transport [9,10], and the ionization probability of atoms exposed to strong electromagnetic fields [11]. In semiconductors, approximate energy gaps calculated in DFT often drastically underestimate the experimental gap [13,14]. In Mott insulators particular, the entire gap is due to Δ_{xc} [3,12]. Recently it was pointed out that a similar discontinuity problem can also appear in the spin-DFT calculation of spin gaps in materials relevant for spintronics [15]. The question whether the neglect of Δ_{xc} or the error in $E_g^{KS,approx}$ is responsible for the underestimate of the band gap in solids is considered in a standard textbook in the field to be '*of tremendous practical importance*' [1], and the calculation of Δ_{xc} is ranked in a recent monograph as '*certainly one of the major outstanding problems in contemporary DFT*' [16], but no general answer is known.

In the present paper we draw attention to an alternative representation of Δ_{xc}, which casts it not as a derivative discontinuity but as a difference of single-particle eigenvalues, similar to the KS gap. We point out that this relation provides a simple physical interpretation of the elusive xc discontinuity, and use it to estimate xc discontinuities of light atoms. The resulting correction Δ_{xc}^{est} substantially improves agreement with experimental fundamental gaps, reducing the error by more than a factor of 10. To show that the proposed scheme remains viable for more complex systems, we also present data on trans-polyacetylene (tPAC).

Table 1
Experimental gap, $E_g^{exp} = I^{exp} - A^{exp}$, KS HOMO-LUMO gap, E_g^{KS}, and KS gap corrected by adding our estimate for the discontinuity, $E_g^{DFT} = E_g^{KS} + \Delta_{xc}^{est}$, for atoms Li ($Z = 3$) to Mg ($Z = 12$), with exception of the nobel gases. The values for Δ_{xc}^{est} were obtained from Eq. (7) using the BLYP functional and the 6-311G(d) basis set. All data in eV.

Z	3	4	5	6	7	8	9	11	12
	Li	Be	B	C	N	O	F	Na	Mg
E_g^{KS}	1.40	3.56	0.614	0.598	3.76	0.860	0.820	0.917	3.38
E_g^{DFT}	4.59	9.01	8.12	10.1	14.4	13.2	15.1	4.42	7.19
E_g^{exp}	4.77	9.32	8.02	10.0	14.5	12.2	14.0	4.59	7.65

The basic formula follows from the fact that I and A can be calculated in DFT not only from ground-state energies, but also from single-particle eigenvalues, according to $I = -\epsilon_N(N)$ and $A = -\epsilon_{N+1}(N+1)$ (the analogue of Koopmans' theorem in DFT) [1,17]. By using these relations and the definition of E_g^{KS} one finds, upon combining Eqs. (4) and (5) [18],

$$E_g = \epsilon_{N+1}(N) - \epsilon_N(N) + \Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_N(N), \tag{6}$$

which implies

$$\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) = A_{KS} - A. \tag{7}$$

In the last step we used the fact that the affinity of the KS system, A_{KS}, is simply the negative of the energy of the lowest unoccupied orbital. The extreme right-hand-side of Eq. (7) provides an intuitive interpretation of the discontinuity: in an interacting system, the electrons repell, hence the energy cost of removing the outermost electron from the negative species (which is measured by the electron affinity) is reduced, $A < A_{KS}$, and a positive Δ_{xc} results. In the following, we exploit Eq. (7) to calculate Δ_{xc} for atoms and semiconducting polymers. This procedure requires only two self-consistent calculations, and obtains Δ_{xc} as a difference of two numbers of size much closer to Δ_{xc} itself than $E(N)$.

If the right-hand side of Eq. (7) could be calculated exactly, this procedure would determine the exact xc discontinuity. An estimate of Δ_{xc} is thus obtained by using in (7) the KS eigenvalues obtained in two approximate KS calculations, one for the neutral species, the other for the anion. Note that Eq. (7) casts Δ_{xc} as a difference of two affinities, and while each normally is predicted wrongly by common functionals (e.g., due to self-interaction errors), one may expect a large degree of error cancellation between both, leading to much better values for the difference than for each affinity individually. We

Table 2
As in Table 1, but for elements Al ($Z = 13$) to Ca ($Z = 20$). The last column is the root-mean-square (rms) error obtained for all listed atoms, $Z = 3$ to $Z = 20$. This error is drastically reduced by including our estimate of the discontinuity.

Z	13 Al	14 Si	15 P	16 S	17 Cl	19 K	20 Ca	rms error
E_g^{KS}	0.272	0.188	2.01	0.215	0.146	0.601	2.36	7.67
E_g^{DFT}	5.09	6.43	8.45	7.64	8.88	3.63	5.32	0.606
E_g^{exp}	5.55	6.76	9.74	8.28	9.36	3.84	6.09	-

call this calculation an estimate, and not an approximation, to stress that it exploits an error cancellation that is hard to quantify *a priori*. However, we find that this estimate yields results that are in quantitative agreement with independent alternative calculations and with experiment.

Tables 1 and 2 compare, for 16 light atoms, the experimental gap, the KS HOMO-LUMO gap, and the DFT gap, defined as the sum of the KS gap and the estimated xc discontinuity. The KS calculations were performed with the `GAUSSIAN 98` [19] program, and selected results were confirmed by calculations with `GAUSSIAN 03` and `GAMESS`. The influence of the choice of the xc functional and of the basis set on the value of Δ_{xc} will be explored in a separate publication. Here, we use the B88-LYP functional and the $6-311G(d,p)$ basis set. The tables show that the error of the KS gap is significantly and consistently reduced by adding the estimated xc discontinuity to the KS gap, dropping by more than an order of magnitude — from $7.67eV$ to $0.606eV$ — over the data set in Tables 1 and 2. This large drop, together with the fact that the improvement is systematic (obtained not only on average, but in every individual case), strongly suggests that (7) is a reliable and useful way of obtaining the discontinuity.

Specifically for the Be atom, we can further compare with independent theoretical expectations, because the discontinuity of this atom has previously been estimated by Jones and Gunnarsson (JG) [20] from numerically exact KS eigenvalues, obtained earlier by Pedroza and Almbladh [21] from CI densities and inversion of the KS equation. Our value $\Delta_{xc}^{Be} = 5.5eV$ is encouragingly close to $\Delta_{xc}^{Be,JG} = 5.7eV$, but does not require CI densities, numerical inversion of the KS equations, or experimental input, all of which went into the estimate $\Delta_{xc}^{Be,JG}$.

Figure 1 is a plot of the data in the tables, revealing that Δ_{xc} roughly follows the atomic shell structure. Particularly small discontinuities are found for atoms with one electron outside a closed shell, such as Li and Na. The largest discontinuities are, however, not observed for closed-shell systems but for systems one electron short of a closed shell, as is seen comparing F with

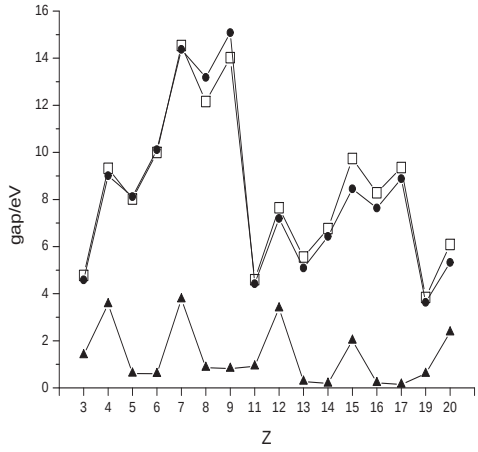

Fig. 1. Plot of the data in Tables 1 and 2: Kohn-Sham HOMO-LUMO gap (triangles), experimental fundamental gap (open squares) and Kohn-Sham HOMO-LUMO gap corrected by adding our estimate for the discontinuity (full circles), for 16 light atoms. The lines are only guides for the eye.

Ne or Cl with Ar. We interpret this by means of Eq. (7) as a consequence of the fact that Δ_{xc} is related to two affinities, which involve negative species with one additional electron, leading to a closed shell for F^- and Cl^-.

To investigate the applicability of the proposed procedure to more complex systems, for which CI calculations are out of question, we show in Fig. 2 the xc discontinuity of tPAC. Figure 2 shows that for small oligomers the size of the discontinuity is comparable to that observed in atoms. For medium sized chains, the discontinuity is reduced, and the resulting corrected gap is in the range $1.5 - 3.5eV$, depending on the number of monomers. Calculated gaps of isolated tPAC chains (see Refs. [23,24] and references therein) range from $1.6eV$ to $6.1eV$. Clearly, our estimate of the corrected gap in isolated finite chains is consistent with this range, whereas the uncorrected KS gap is not. On increasing the monomer number M, our estimates of Δ_{xc} and E_g extrapolate to 0 approximately as $1/M$. This tendency is consistent with experiments for small oligomers [22], but not with the possibly nonzero gap of an infinite chain. Clearly, as $M \to \infty$ the small energy change upon adding a single electron gradually becomes numerically inperceptible, and our estimate should not necessarily be trusted for large extended systems. A more detailed analysis of the gap structure of tPAC, a variety of methodological variations of our basic procedure, and further work on atoms and polymers, will be presented in a future publication.

In summary, we have cast the derivative discontinuity of DFT as a difference of two affinities, Eq. (7), and used approximate calculations of these to obtain estimates for the discontinuity in light atoms and in a series of polyacetylene

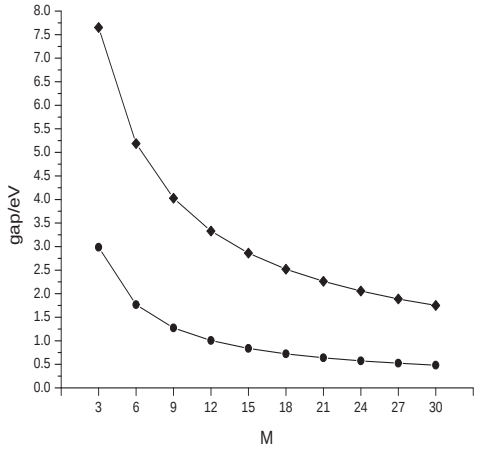

Fig. 2. KS HOMO LUMO gap (lower curve) and corrected DFT gap (upper curve), for tPAC fragments as a function of monomer number M, obtained from Eq. (7) form the BLYP functional and the 6-311G(d,p) basis set. The lines are only guides for the eye.

oligomers. Our results are consistent with previous results for atoms and for polymer chains, and significantly and consistently reduce the error between calculated and measured fundamental gaps.

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References

[1] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).

[2] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[3] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[4] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[5] W. Kohn, Phys. Rev. B **33**, 4311 (1986).

[6] A. Görling and M. Levy, Phys. Rev. A **52**, 4493 (1995).

[7] A. Wasserman, N. T. Maitra and K. Burke, Phys. Rev. Lett. **91**, 263001 (2003).

[8] D. J. Tozer and N. C. Handy, J. Chem. Phys. **109**, 10180 (1998).

[9] D. J. Tozer, J. Chem. Phys. **119**, 12697 (2003).

[10] Q. Wu and T.V. Voorhis, Phys. Rev. A **72**, 024502 (2005).

[11] M. Lein and S. Kümmel, Phys. Rev. Lett. **94**, 143303 (2005).

[12] N. A. Lima, L. N. Oliveira, and K. Capelle, Europhys. Lett. **60**, 601 (2002).

[13] R. W. Godby, M. Schlüter and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

[14] M. Grüning, A. Marini and A. Rubio, J. Chem. Phys. **124**, 154108 (2006).

[15] K. Capelle and G. Vignale, Phys. Rev. Lett. **86**, 5546 (2001).

[16] G. F. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge University Press, 2005).

[17] Q. Wu, P. W. Ayers, and W. Yang, J. Chem. Phys. **119**, 2978 (2003).

[18] L. J. Sham and M. Schlüter, Phys. Rev. B **32**, 3883 (1985).

[19] *Gaussian 98*, M. J. Frisch et al., Gaussian Inc., Pittburgh, PA (1998).

[20] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[21] C.-O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).

[22] C. R. Fincher et al., Phys. Rev. B **20**, 1589 (1979).

[23] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **82**, 1959 (1999).

[24] S. Rohra, E. Engel and A. Görling, Phys. Rev. B **74**, 045119 (2006).